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Chemical Shift driven Molecular Dynamics and Structure Optimization

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Common NMR measurements provide three kinds of structural information: J-coupling constants between nuclei separated by bonds which reflects the size of dihedral angles, nuclear Overhauser enhancement intensities corresponding to interproton distances and chemical shifts containing the whole nearby electronic structure information.

We represent a chemical shift driven molecular dynamics and geometry optimisation for structure investigation. This method needs energy gradients every step either during a molecular dynamics or a geometry optimisation. In order to calculate forces very fast a new developed universal force field with fluctuating charges is used. Additionally to the molecular force field correcting contributions, pseudo forces, due to chemical shift deviations of experimental and calculated values are introduced. Chemical shift values attributed to corresponding atoms are considered for correction. These pseudo forces need to be calculated every time step. Hence an effective method for obtaining theoretical chemical shifts of atoms are needed. For this we tread a semiempirical bond polarisation theory. In this theory the chemical shift depends on all other charged sites around. The chemical shift is proportional to the quantum chemical polarisation energies of all located bond orbitals (χ) due to surrounding charged sites (q). The formula for the isotropic chemical shift (σ) is given as:

$$\sigma_a = \sum_i \left(\delta^0_{ab_i} + \delta_{ab_i}{}^1 \sum_x \left(\left\langle \chi_{a_i} \left| \frac{q_x}{|R_{a_i,x} - r|} \right| \chi_{a_i} \right\rangle - \left\langle \chi_{b_i} \left| \frac{q_x}{|R_{b_i,x} - r|} \right| \chi_{b_i} \right\rangle \right) \right)$$

The proportionality factors (δ^0, δ^1) are obtained for ^{13}C bonded to Hydrogen, Oxygen and Nitrogen.

We represent a ^{13}C chemical shift structure investigation on the pseudo peptide Bz-His-(N-CH_2-CH_2-NH_2)Gly-His-NH_2 and its Zn-complex: